

## Flexible magnetic coordination networks sensitive to guest molecules

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Structurally flexible coordination networks that react to different external stimuli with structure deformation, and consequently changes in magnetic properties, are potential candidates for molecular switches and sensors. The design of guest-sensitive molecular magnetic materials based on the specific building blocks:  $[\text{Ni}(\text{cyclam})]^{2+}$  (cyclam = 1,4,8,11-tetraazacyclotetradecane) cation and polycyanometallate anions is discussed. The examples of different dimensionality networks and the changes in their structure and magnetic properties in response to sorption of small molecules are presented.

**Keywords:** coordination polymers, molecular magnets, polycyanometallates, advanced materials

### I. INTRODUCTION

Many devices of everyday use, from hair driers and vacuum cleaners to computers and ATMs, require magnetic materials. Traditional magnets are metal alloys or metal oxides. They are heavy, non-transparent and often sensitive to corrosion, which limits their applications. Moreover, they are produced in high-temperature energy-consuming processes. Modern material science is looking for new molecule-based magnets, in which different physical properties can be merged. **Multifunctional molecular materials combining magnetism with other properties may turn out essential in the development of future technologies.** A little while ago it was unimaginable that light, gleaming in the dark magnets would be within reach - now they are synthesized in chemical laboratories. In order to design a multifunctional material it is necessary to link molecular fragments called building blocks, which exhibit desired properties. The characteristics of the resulting molecular system depend on the properties of the respective building blocks and the way they are connected. It is possible to unite different physical attributes like chirality or luminescence with magnetism in order to obtain optically-active, and/or light-emitting magnets [1]. One of very interesting features that can be achieved in magnetic coordination networks is their ability to react to different external stimuli such as the presence of guest molecules, temperature and pressure changes or irradiation. The response in form of the change in magnetic, optical or electrical properties makes such materials good candidates for molecular switches and sensors. There are several different phenomena which can trigger such stimulus-response mechanism in molecular materials, including spin-crossover [2], charge-transfer [3] and topotactic reactions [4]. There is also an interesting group of compounds, characterised by the flexible coordination skeleton, in which changes in magnetic properties are caused by the relatively small deformation of the structure, restricted to the modifications of bond lengths and angles. Such flexible coordination networks react, often reversibly, to the sorption of guest molecules, temperature or pressure. The construction of this type of materials requires the use of certain type of building blocks. They must form strong but bendable coordination bonds, which can effectively mediate magnetic exchange. At the same time they should afford only weak intermolecular interactions to allow the network to adapt freely to changing conditions. The inclusion of guest molecules is facilitated by the presence of void spaces in the structure. Porosity requires long linkers between framework nodes. In porous metal-organic-frameworks (MOF) it is achieved by the

use of long organic bridging ligands [5]. However, since for effective magnetic interactions short distances between paramagnetic centres are needed, in the construction of porous magnetic networks linear paramagnetic linkers must be employed.

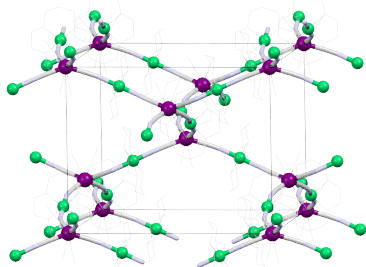
Here we present some examples of structurally flexible magnetic networks sensitive to sorption of water and other small molecules. The systems show different dimensionalities from 1D to 3D, but they are all based on the specific type of building blocks:  $[\text{Ni}(\text{cyclam})]^{2+}$  complex (cyclam = 1,4,8,11-tetraazacyclotetradecane) as a cation and polycyanometallates  $[\text{M}(\text{CN})_n]^{m-}$  of different transition metals as anions. Cyclam is a macrocyclic ligand that forms a very stable complex with  $\text{Ni}(\text{II})$ , taking up equatorial positions in an octahedral structure. The presence of labile axial ligands ensures that it acts as a linear paramagnetic cationic linker with spin  $s = 1$ . Moreover, cyclam takes up relatively little space and its aliphatic chains interact only weakly with neighbouring molecules. Polycyanometallates provide CN ligands which link metal centres and mediate relatively strong magnetic interactions [6]. Cyano-bridges are usually very stable, but at the same time bendable, and most importantly the M-N-C angle strongly influences the nature and the strength of magnetic exchange.

### II. COMPOUNDS AND THEIR CHARACTERISTIC

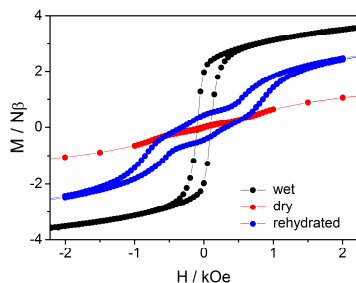
#### 1. 3D water sensitive $\text{Ni}^{\text{II}}$ - $\text{Nb}^{\text{IV}}$ diamond-like network

The  $\{[\text{Ni}(\text{cyclam})]_2[\text{Nb}(\text{CN})_8]\}_n$  [7] compound is formed as a powder in the spontaneous reaction of  $[\text{Ni}(\text{cyclam})]^{2+}$  and  $[\text{Nb}(\text{CN})_8]^{4-}$  in water solution. The crystalline product cannot be obtained due to the decomposition of the  $[\text{Nb}(\text{CN})_8]^{4-}$ , however it was assigned 3D diamond-like topology on the basis of an analogical compound based on W(IV) (Figure 1). The proposed structure is characterised with a net of channels filled with crystallisation water. The wet sample directly from synthesis exhibits long range ferromagnetic ordering with critical temperature  $T_c = 11.8$  K and magnetic hysteresis typical for soft ferromagnets at 2 K (Figure 2). Upon drying the  $T_c$  value drops below 2K and the hysteresis loop closes. The sample can be subsequently rehydrated by immersion in water, but the process does not restore the original phase, probably due to the permanent closing of channels in selected directions. The compound becomes a metamagnet, characterised by different

strength of magnetic interactions in different directions. The magnetic hysteresis reappears with characteristic inflection points. These observations prove that the network exhibits structural flexibility and undergoes structural and magnetic changes upon the loss of water. However, the process of dehydration does not show full reversibility, which is essential for potential applications.



**Fig. 1** Proposed diamond-like structure of  $\{[\text{Ni}(\text{cyclam})_2][\text{Nb}(\text{CN})_8]_n\}$ ; green balls: Ni, purple balls: Nb, thick lines: CN bridges, thin lines: cyclam and terminal cyanides; water molecules and hydrogen atoms omitted for clarity.

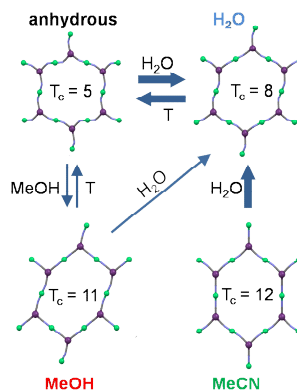


**Fig. 2** Magnetization vs. field plot at 2K for  $\{[\text{Ni}(\text{cyclam})_2][\text{Nb}(\text{CN})_8]_n\}$ .

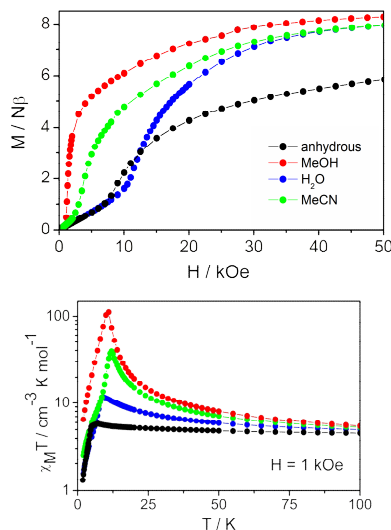
## 2. 2D microporous $\text{Ni}^{\text{II}}$ - $\text{W}^{\text{V}}$ honeycomb-like network

The compound based on  $[\text{Ni}(\text{cyclam})]^{2+}$  and  $[\text{W}(\text{CN})_8]^{3-}$  of the formula  $\{[\text{Ni}(\text{cyclam})][\text{W}(\text{CN})_8]_2\}_n$  is a 2D honeycomb-like network [8]. Its structure is characterized by channels of ca. 0.5 nm diameter running across the layers. In the hydrated form, which is stable under ambient conditions, the channels are filled with crystallisation water. When heated above 40°C the compound undergoes fully reversible dehydration accompanied by single-crystal-to-single-crystal transformation (Figure 3). The network can also accommodate larger guest molecules. Methanol - (MeOH) [9] and acetonitrile - (MeCN) [10] modified forms can be obtained directly from synthesis in appropriate solvent mixtures. MeOH can also be reversibly introduced by the sorption into anhydrous phase. For all the forms structural characterisation was possible, and the results show marked flexibility of the coordination skeleton, but no changes in bonding. The deformation of hexagonal rings of the network is clearly visible in Figure 3, which also shows existing interconversion pathways. All the forms are metamagnets, which is typical for layered structures, where interactions through bonds are stronger and often ferromagnetic, while those between layers are weak and antiferromagnetic. However, all the forms significantly differ in magnetic properties (Figure 4),

which is reflected in different critical temperatures of antiferromagnetic ordering (from 5 K for anhydrous to 12 K for MeCN form) and critical field of metamagnetic phase transition (from 11.5 kOe for hydrated to 1.2 kOe for MeOH form). In the anhydrous phase the ring is shrunken and the cyano-bridges are bent. It results in antiferromagnetic interactions between one of the Ni ions and its W neighbours and apparently lower saturation magnetisation. Larger guest molecules cause the ring expansion and straightening of bridges, which results in stronger ferromagnetic interactions and higher  $T_c$ . At the same time MeOH and MeCN, which are less polar than water and form weaker H-bonds, penetrate the space between the layers pushing them apart, which weakens the inter-layer antiferromagnetic interactions, hence lower  $H_c$  values for these forms. This network presents enormous flexibility and presents a model structure of the sorption-switchable molecular magnet.



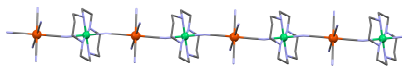
**Fig. 3** Structural transformation pathways of  $\{[\text{Ni}(\text{cyclam})_3][\text{W}(\text{CN})_8]_2\}_n$ , view parallel to the channels. Only metal centers and cyano-bridges are presented for clarity; green balls: Ni, purple balls: W, grey sticks: C, blue sticks: N. Bold arrows denote single-crystal-to-single-crystal transformations.



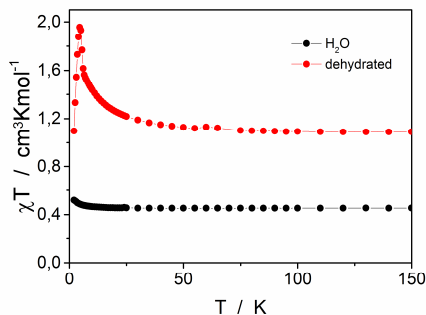
**Fig. 4** Magnetization vs. field plot at 2K (top), and temperature dependence of magnetic susceptibility (bottom) for  $\{[\text{Ni}(\text{cyclam})_3][\text{W}(\text{CN})_8]_2\}_n$ .

### 3. 1D Ni - Fe chain with hydration switchable charge-transfer

The cyclam ligand has an additional asset of stabilising higher oxidation states of several metals. Therefore  $[\text{Ni}^{\text{II}}(\text{cyclam})]^{2+}$  is relatively easily oxidised to  $[\text{Ni}^{\text{III}}(\text{cyclam})]^{3+}$ . The later complex was used to construct CN-bridged  $\{(\text{H}_3\text{O})[\text{Ni}^{\text{III}}(\text{cyclam})][\text{Fe}^{\text{II}}(\text{CN})_6] \cdot 5\text{H}_2\text{O}\}_n$  chain [11] (Figure 5), in which the unusual oxidation states of metal centres are stabilised by the presence of acid. The compound can be dehydrated to a monohydrate in a reversible process, although accompanied by gradual decomposition. The effect of the dehydration is a charge-transfer process in the redox couple  $\text{Ni}^{\text{III}}\text{-Fe}^{\text{II}} \rightarrow \text{Ni}^{\text{II}}\text{-Fe}^{\text{III}}$ , which results in the formation of  $\text{Ni}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  in about 40% of metal centres. It causes change of colour from dark blue to brownish-green and marked change in magnetic susceptibility in the entire temperature range (Figure 6). The hydrated form is a typical paramagnet due to the isolation of paramagnetic Ni(III) centres by diamagnetic NC-Fe(II)-CN fragments. In the dehydrated phase intra-chain ferromagnetic interactions arise. The hydration-switchable charge-transfer effect is very rare and for magnetic CN-bridged systems was observed only once before. Moreover, new research results indicate that the described redox system can be modified towards better stability and sensitivity to additional stimuli, like temperature changes.



**Fig. 5** Fragment of the  $\{(\text{H}_3\text{O})[\text{Ni}^{\text{III}}(\text{cyclam})][\text{Fe}^{\text{II}}(\text{CN})_6] \cdot 5\text{H}_2\text{O}\}_n$  structure; orange balls: Fe, green balls: Ni, grey sticks: C, blue sticks: N; water molecules and hydrogen atoms omitted for clarity.



**Fig. 6** Temperature dependence of magnetic susceptibility of  $\{(\text{H}_3\text{O})[\text{Ni}^{\text{III}}(\text{cyclam})][\text{Fe}^{\text{II}}(\text{CN})_6] \cdot 5\text{H}_2\text{O}\}_n$  at 1 kOe.

### III. CONCLUSION

The macrocyclic complex  $[\text{Ni}(\text{cyclam})]^{2+}$  was used to construct cyano-bridged bimetallic coordination networks of different dimensionality with respective polycyanometallates. All the presented compounds exhibit marked flexibility of the framework, which is sensitive to inclusion/removal/exchange of small guest molecules. It affords deformations in the structure and therefore changes in the magnetic behavior. In the case of Ni-Fe 1D system a rare effect of dehydration-induced metal-to-metal charge-transfer was observed. Recent research results indicate that it is possible to modify this material to increase its stability and gain additional control of the redox process by temperature changes. Moreover, introduction of non-coordinated ions allows the control network dimensionality. The presented family of compounds due to their sorption-sensitive properties shows a great potential in the development of molecular sensors and multi-controllable switches.

- [1] D. Pinkowicz *et al.*, Science Progress, 2011, **94**(2), 139-183
- [2] J. Cicera, Rev. Inorg. Chem., 2014, **34**, 199-216
- [3] N. Ozaki *et al.*, New J. Chem., 2014, **38**, 1950-1954
- [4] D. Pinkowicz *et al.*, Angew. Chem. Int. Ed., 2011, **50**, 3973-3977
- [5] H. Furukawa *et al.*, Science, 2013, **341**, 1230444
- [6] H. Tokoro *et al.*, Dalton Trans. 2011, **40**, 6825-6833
- [7] B. Nowicka *et al.*, Dalton Trans., 2013, **42**, 2016-2021
- [8] B. Nowicka *et al.*, Inorg. Chem., 2007, **46**, 8123-8125
- [9] B. Nowicka *et al.*, Dalton Trans., 2011, **40**, 3067-3073
- [10] B. Nowicka *et al.*, CrystEngComm, 2015, **17**, 3526-3532
- [11] B. Nowicka *et al.*, Chem. Comm., 2015, **51**, 11485-11488